U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-298 543

Sampling and Analysis of Atmospheric Sulfates and Related Species

(U.S.) Environmental Sciences Research Lab, Research Triangle Park, NC

5 Oct 77

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	PB 298543
EPA-600/J-78-119	JOURNAL ARTICLE	

4. TITLE AND SUBTITLE
SAMPLING AND ANALYSIS OF ATMOSPHERIC SULFATES AND RELATED SPECIES

5. REPORT DATE

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
R.K. Stevens, T.G. Dzubay, G. Russwurm,* and D. Rickel*
*Northrop Services, Inc., RTP, NC

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
(Same as Block 12)

10. PROGRAM ELEMENT NO.
1AD712

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Sciences Research Laboratory -- RTP, NC
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA/600/09

15. SUPPLEMENTARY NOTES
REFERENCE: Atmos. Environ., 12(1-3):55-68, 1978.

16. ABSTRACT

Sampling and analytical methods to measure atmospheric concentrations of sulfur, sulfates and related species are compared for aerosols collected in New York City, Philadelphia, Pa., South Charleston, W.VA., St. Louis, Mo., Glendora, Calif., and Portland, Ore. For the aerosol sampling, dichotomous samplers that were equipped with virtual impactors were used to separately collect fine ($< 3.5\mu m$) and coarse ($>3.5\mu m$) particles on membrane filters. Both size fractions were analyzed by energy dispersive x-ray fluorescence spectroscopy to determine the total amounts of sulfur and other elements, and the samples were anlayzed by an Ion Chromatograph and by the thorin titration method to determine sulfate. These analyses reveal that more than 70% of the sulfur occurs in the fine particle fraction for at least 90% of the samples. Sulfate typically accounts for about 40% of the mass of the fine particle fraction, and in some instances it accounts for more than 50%. For the fine particle fraction , the ratio of the sulfate and the sulfur mass concentrations is 3.04 ± 0.15, which is in excellent agreement with the value of 3.00 for sulfate. To test for the existence of sulfite ions in the samples, a cold extraction procedure was developed, which minimizes the conversion of sulfite to sulfate. Analysis for sulfite using the Ion Chromatograph indicates that less than 2% of the sulfur collected in South Charleston, W.Va. and Philadelphia, Pa. is in the form of sulfite.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air pollution		13B
*Aerosols		07D
*Sulfates		07B
*Sampling		14B
*Chemical Analysis		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	16
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	A02 - A01

EPA Form 2220-1 (9-73)

REPRODUCED BY
NATIONAL TECHNICAL INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA-600/J-78-119
JOURNAL ARTICLE

Atmospheric Environment Vol. 12, pp. 55–68. Pergamon Press 1978. Printed in Great Britain.

SAMPLING AND ANALYSIS OF ATMOSPHERIC SULFATES AND RELATED SPECIES

ROBERT K. STEVENS and THOMAS G. DZUBAY
U.S. Environmental Protection Agency Research, Triangle Park, NC27711, U.S.A.

and

GEORGE RUSSWURM and DWIGHT RICKEL
Northrop Services, Inc., Research Triangle Park, NC27709, U.S.A.

(*First received* 13 *July* 1977 *and in final form* 5 *October* 1977)

Abstract—Sampling and analytical methods to measure atmospheric concentrations of sulfur, sulfates and related species are compared for aerosols collected in New York City; Philadelphia, PA; South Charleston, WV; St. Louis, MO; Glendora, CA; and Portland, OR. Dichotomous samplers equipped with virtual impactors were used to separately collect fine ($<3.5\ \mu m$) and coarse ($>3.5\ \mu m$) particles on membrane filters. Both size fractions were analyzed by energy-dispersive X-ray fluorescence spectroscopy to determine the total amounts of sulfur and other elements, and the samples were analyzed by an Ion Chromatograph and by the thorin spectrophotometeric method to determine sulfate. These analyses reveal that more than 70% of the sulfur occurs in the fine particle fraction for at least 90% of the samples. Sulfate typically accounts for about 40% of the mass of the fine particle fraction, and in some instances it accounts for more than 50%. For the fine particle fraction, the ratio of the sulfate and the sulfur mass concentrations is 2.96 ± 0.15, which is in excellent agreement with the value of 3.00 for sulfate.

To test for the existence of sulfite ions in the samples, a cold extraction procedure was developed, which minimizes the conversion of sulfite to sulfate. Analysis for sulfite using the Ion Chromatograph indicates that less than 2% of the sulfur collected in South Charleston, WV, and Philadelphia, PA, is in the form of sulfite.

A procedure was developed to preserve the acidity of aerosols collected with an automated dichotomous sampler and was recently used to sample aerosols in Research Triangle Park, NC. Analysis of the samples for H^+, NH_4^+, and SO_4^{2-} ions revealed that the sulfate concentrations were typically 10 to 14 μg^{-3} and that H^+ ions accounted for 5 to 60% of the cations associated with sulfate. In addition the sum of NH_4^+ and H^+ equalled the SO_4^{2-} concentration expressed in nanoequivalents.

In the network of stations that was part of the Regional Air Pollution Study (RAPS) the hi-volume sampler gave mass and sulfate concentrations that were consistently higher than values obtained for the automated dichotomous sampler. For samples collected at eight RAPS stations at St. Louis, MO, between September and December 1975, the ratio for sulfate determined for the two types of samplers was 1.32.

INTRODUCTION

Although sulfates have long been known to exist in the atmosphere, reliable sampling and analytical methods to determine their physical and chemical form have not been readily available until recently. For the past 5 years the U.S. Environmental Protection Agency (EPA) has supported projects to develop procedures to collect aerosols in a manner that minimizes artifact formation and to separate the respirable particles (particles $<3.5\ \mu m$ in aerodynamic diameter) from larger particles. The instrumentation that now appears to satisfy these sampling requirements is based on the virtual impactor principle (Conner, 1966) and has been engineered into what has been termed the dichotomous sampler. Both automated and manual versions of the dichotomous sampler have been used in several field studies across the United States. The samples have been analyzed to determine mass, sulfate, nitrate, ammonium ion, hydrogen ion, and elemental composition. The results from these field studies confirm the limited observations of Weiss (1976) that sulfur was the predominant component in the submicron aerosol in the United States.

Concurrent with the development of these samplers was the development of an energy dispersive X-ray fluorescence (EDXRF) system (Jacklevic, 1974, 1976, 1977) and their application to the analysis for as many as 35 elements contained in particles collected on membrane filters with dichotomous samplers (Dzubay, 1975; Loo, 1976; Dzubay *et al.*, 1977).

Because EDXRF only measures elemental composition, additional methods were developed to characterize the chemical form of the samples. Brosset (1976) developed methods to measure the H^+, NH_4^+, and SO_4^{2-} concentrations in aerosols. Recent developments in ion exchange chromatography (Small, 1976) have led to a commercial instrument, the Ion Chro-

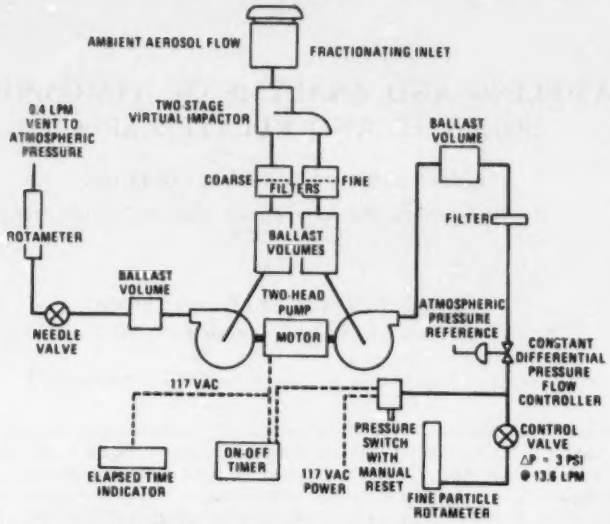

Fig. 1. Schematic view of dichotomous sampler with constant flow rate system having a pressure regulator to maintain a constant pressure differential across a fixed orifice.

matograph*, which simultaneously measures Cl^-, Br^-, SO_3^{2-}, NO_3^-, and SO_4^{2-} (Mulik, 1976). In the present text the analytical capabilities of these methods are compared. The comparison consists of the analysis of aerosols collected in New York City; Philadelphia, PA; South Charleston, WV; St. Louis, MO; Glendora, CA; and Portartland, OR.

These studies not only serve as a basis for selecting sampling and analytical methodology to determine sources of atmospheric sulfates but also demonstrate the importance of automated aerosol sampling for periods of less than 3 hours. Short term sampling and analysis are made possible both by the development of reliable automated aerosol size-fractionation devices and by the improved sensitivity and specificity of methods to measure sulfates and related species.

EXPERIMENTAL

Sampling

Manual dichotomous samplers (MDS) fabricated by Environmental Research Corporation, St. Paul, MN (Stevens, 1975; Dzubay, 1975; Dzubay *et al.*, 1977), were used for field studies in New York City; Philadelphia, PA; South Charleston, WV; and Portland, OR. The samplers were operated at flow rates of 14 l. min^{-1}, and the sampling periods ranged from 24 h in South Charleston to 2 h in New York City. A network of 10 automated dichotomous samplers (ADS) fabricated by Lawrence Berkeley Laboratory (Goulding, 1975; Loo, 1976) was used for the St. Louis studies (Meyers, 1975). The flow rate for the ADS was 50 l. min^{-1}, and the sampling intervals ranged from 2 to 12 h. An ADS was also operated in Glendora, CA, where samples were collected every 6 h. For the MDS the aerosol particles were collected on 37 mm diameter FALP Fluoropore filters (Millipore Corp., Bedford, MA), which consist of 1 μm pore-size Teflon† membranes bonded to a polyethylene support net. In the ADS the filters that were used had 1.2 μm pores and were made of esters of cellulose (Millipore). Fluoropore filters could not be used in the ADS because the polyethylene support net prevented the filters from being adequately sealed in the filter holder.

In the MDS that was operated in Philadelphia, a pneumatic flow rate controller of the type shown in Fig. 1 was used to maintain a constant sampling flow rate. An inexpensive differential pressure regulator (Moore Products Co., Houston, TX, Flow Controller CG-63BD) in the exhaust line of the pump maintained a constant pressure differential across a fixed orifice and thereby maintained a constant flow rate through the system. The differential flow control system has been tested over a -20 to $+40$°C temperature range, and the flow rate varied less than 5%. In the manual dichotomous samplers operated at the other sites, a Sierra flow controller (Sierra Corp., Carmel Valley, CA), consisting of an anemometer sensor and a variable-speed pump, was used to maintain a constant flow rate. Tests have shown that both types of flow control systems are capable of maintaining the flow rate constant to better than 5% for pressure drops up to 25 cm Hg across the filter.

For other studies designed to measure the H^+ content, an ammonia denuder was coupled to a special ADS sampler fabricated by Cabot Corporation (Billerica, MA). The denuder, shown in Fig. 2, is composed of 16 glass tubes (30 cm length, 0.5 cm i.d.) arranged in parallel and coated with phosphorous acid. The coating was applied by inserting approximately 300 mg of H_3PO_3 into the end of each tube and gently warming and rotating the tube to coat the walls evenly. The efficiency for the removal of NH_3 was measured by flowing 100 ppb NH_3 through the denuder at relative humidities of 20, 50 and 80% and measuring the exit concentration with a chemiluminescent NH_3 monitor (Hodgeson, 1971). The measured denuder efficiency was in agreement with the calculated values of 99.9%. For the acid measurements, the aerosol collection surface consisted of unbacked 1 μm Teflon membrane filters. After the aerosol samples were collected, they were stored in a NH_3 free atmosphere at 20 to 50% relative humidity to prevent neutralization and volatilization of sulfuric acid in the sample.

* Mention of product or company name is not intended as an endorsement by the US Environmental Protection Agency.

† Registered trademark of E.I. DuPont De Nemours & Company, Inc., Wilmington, DE.

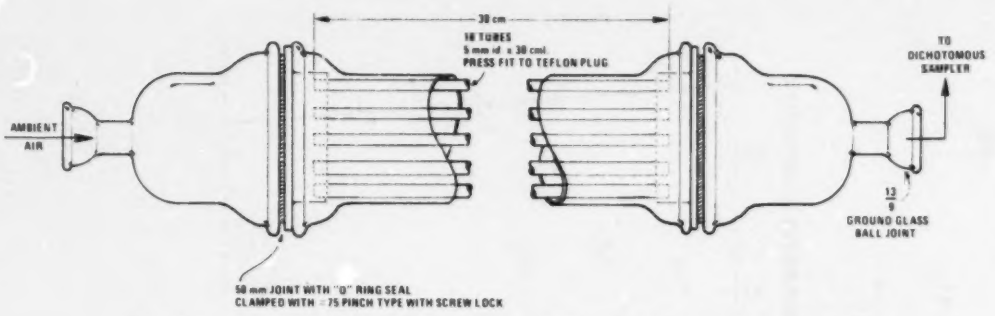

Fig. 2. Cross sectional view of NH_3 gas diffusion denuder used with dichotomous sampler.

X-ray fluorescence analysis

Prior to any chemical extractions, the elemental composition of filter-collected particles was nondestructively measured in our laboratory using an EDXRF spectrometer. In this device, fabricated by the Lawrence Berkeley Laboratory, a pulsed X-ray tube excites a secondary target, which excites the sample with nearly monoenergetic X-rays (Jaklevic, 1974, 1976, 1977; Goulding, 1975). To obtain high sensitivity for a wide range of elements, each sample is excited by means of three different secondary targets. For the K X-rays of elements with atomic numbers in the ranges 13–20, 21–38 and 39–56 the secondary targets consist of titanium, molybdenum and samarium, respectively. The molybdenum target also excites the L X-rays of lead and other heavy elements. The fluorescent X-rays from the sample are detected using a lithium drifted silicon detector, which uses electronic collimation to minimize the background. Because of a compact geometrical arrangement between components of the spectrometer, an X-ray tube power of only 100 W is sufficient to provide the maximum usable count rate for filter samples.

In applications where the amount of collected particulate matter is expected to be small, it is important to estimate the minimum detectable concentration, C_D. Currie (1977) defines C_D as 3.29 times the standard deviation for determining the background and expresses it as:

$$C_D = 3.29\,\eta^{1/2}(St)^{-1}[tR_b + (\epsilon\, t\, R_b)^2]^{1/2} \qquad (1)$$

where: η = measure of extent to which blank is well characterized (see Currie, 1977). S = sensitivity expressed in counts s^{-1} per ng cm^{-2} for the spectral region containing the full width at half maximum of the peak for the element of interest. t = counting time in seconds. R_b = background in counts s^{-1} for the same spectral region used to determine S for the element. ϵ = relative standard error in determining R_b if errors due to counting statistics were negligible. Assuming that $\epsilon = 0.02$, $\eta = 1$ and $t = 100$ s for each secondary target, values of C_D are given in Table 1 for several elements.

To express C_D in units of ng m^{-3}, one must divide the values in Table 1 by the volume sampled per unit area of filter. For example, this conversion factor is 3.05 m^3 cm^{-2} for 24 h of sampling at a rate of 14 l. min^{-1} through 6.6 cm^2 of filter area. The corresponding C_D value for sulfur is 12 ng m^{-3}. If reasonably accurate information on a certain element is needed, then the concentration C of that element must exceed C_D by at least a factor of 3, to insure that C exceeds the standard deviation by a factor of 10. If one wanted to measure a sulfur concentration of 1 μg m^{-3}, then for the above example, one could shorten the sampling time from 24 to 1 h and still have sufficient sample.

After a sample has been irradiated in our EDXRF spectrometer, the resulting spectrum is analyzed to determine the number of counts that each element contributes. To accomplish this, a least-squares procedure is used to find a linear combination of single-

Table 1. Sensitivities and minimum detectable limits with energy dispersive spectrometer

Element	Secondary target	Sensitivity Counts s^{-1} μg^{-1} cm^2	Background (R_b)	Minimum detectable concentration (C_D), ng cm^{-2}
Al	Ti	7.2	13	203
S	Ti	47	16	36
K	Ti	133	22	16
V	Mo	31	5.8	28
Fe	Mo	67	7.6	15
Sc	Mo	199	2.9	3
Sr	Mo	269	6.9	3.6
Sr	Sm	38	1.7	11.7
Cd	Sm	84	1.8	5.4
Sn	Sm	75	3.5	8.8
Ba	Sm	50	45	74
Pb	Mo	76	3.5	8.6

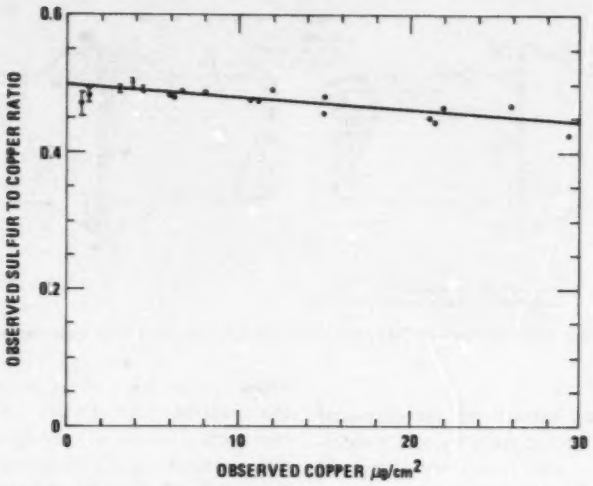

Fig. 3. Ratio of sulfur and copper XRF yields for 0.2 μm copper sulfate deposits of varying mass. The ratios are normalized to 0.505 for zero deposited mass.

element spectra that best describes the unknown spectrum. A library of single-element spectra is obtained for thin standards of each element and is stored in computer memory. The library must contain all elements that could contribute to an unknown sample (Arinc, 1976; Rickel, in press).

The least-squares method is slightly modified for the K X-rays from sulfur to deal with the overlapping M X-rays from lead. Since the concentration of lead can be accurately determined from the emission of L X-rays, it is possible to 'strip' out the interfering lead M peak in the vicinity of the sulfur peak. Such stripping is done prior to performing the least-squares analysis for sulfur. The uncertainty in the result for sulfur because of the presence of lead is estimated to be about 5% of the lead concentration. For example, if the lead concentration were 2 $\mu g\,m^{-3}$, the resulting sulfur uncertainty would be 0.1 $\mu g\,m^{-3}$.

After completion of the spectral analysis, the concentration for each element in the sample is computed from the expression:

$$C = N_i a_i/(F_i A_i) \qquad (2)$$

where: N_i = normalization factor to relate counts to concentration for either sulfur, copper, or tin. i = secondary target designation. a_i = number of counts in the spectrum due to each element. F_i = calibration factor for each element relative to $F_i = 1$ for either sulfur, copper or tin. A_i = attenuation correction factor for the element observed on secondary target i.

The EDXRF spectrometer is calibrated to determine the normalization factors, N_i, for copper and tin using standards that consist of vacuum-evaporated deposits of copper and tin on Mylar films. For sulfur, N_i is determined relative to copper using copper sulfate deposits. The latter were prepared by generating an aerosol of 0.2 μm $CuSO_4 \cdot 5\,H_2O$ particles and collecting the particles on Fluoropore filters. The copper sulfate deposits were prepared in a variety of thicknesses, and the results are shown in Fig. 3. All but the thinnest deposits are thicker than a single monolayer, and the layers of particles attenuate the fluorescent X-rays. To obtain a calibration equivalent to a thin standard, the data in Fig. 3 were least squares fitted with a straight line, which was extrapolated to zero deposit thickness. The sulfur calibration was adjusted so that the y axis intercept is equal to 0.505, which is the sulfur-to-copper mass ratio for copper sulfate.

For the remaining elements, the F factors were determined relative to $F = 1$ for sulfur, copper and tin. Figure 4 shows measured F values using dried solution deposits on 1 $mg\,cm^{-2}$ esters of cellulose membranes obtained from Columbia Scientfic, Inc., Austin, TX, and using vacuum-deposited films obtained from Micromatter Co., Seattle, WA. Figure 4 also shows a smooth curve, which is a fit to the data using a method described by Giauque (1973). The curves were normalized to $F = 1$ for $Z = 16$, 29 and 50. The smooth curve represents an improved calibration since random errors in some of the standards would not significantly affect the curve.

For EDXRF analysis of aerosol particles collected on a membrane filter a correction must be made for any X-ray attenuation by the sample matrix. Such attenuation can occur within individual particles, within layers of particles, and within the filter medium into which particles might penetrate.

Attenuation within individual particles is a small effect for sulfur in the fine particle fraction (Dzubay, 1975); however, a typical aerosol sample consists of layers of particles. The attenuation in such layers can be expressed as:

$$A = [1 - \exp(-\mu_L M/f)]f/\mu_L M \qquad (3)$$

where: M = average mass per unit area, f = fraction

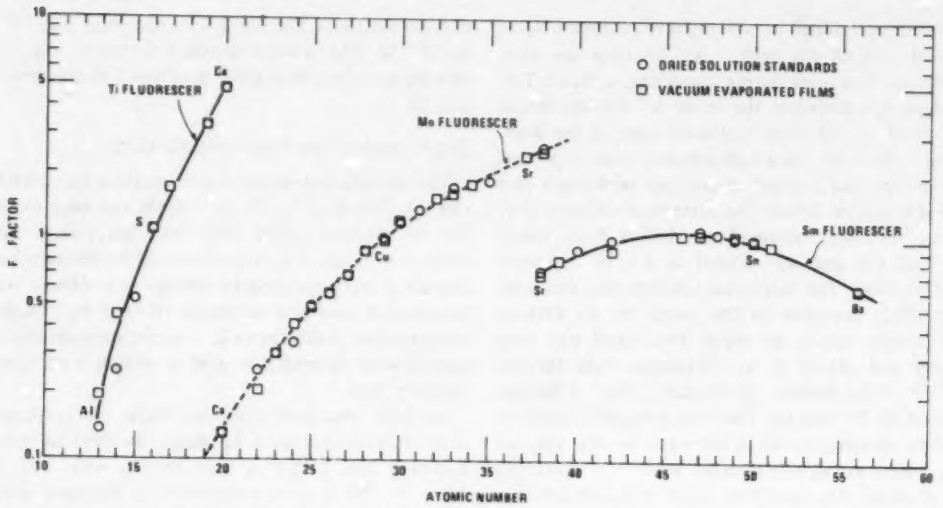

Fig. 4. Calibration data for K X-rays excited using titanium, molybdenum and samarium secondary targets.

of particle deposit area that contains particles, $\mu_L = \mu \sec\theta + \mu' \sec\theta'$, μ,μ' = mass absorption coefficients of incident and fluorescent X-rays in the deposit and θ,θ' = angles between the sample normal and the incident and fluorescent X-ray paths.

The fraction f in Equation 3 is needed to account for any grid pattern or structure in the particle deposit profile. For Fluoropore filters, the polyethylene support net gives a pronounced pattern to the aerosol deposit. By applying Equation 3 to the $CuSO_4$ data in Fig. 3, one deduces the value, $f = 0.45$, for Fluoropore filters. This is consistent with visual observations of aerosol deposits on Fluoropore that indicate that 50 to 60% of the filter is obstructed by the support net.

The mass absorption coefficients are given by the expression:

$$\mu = \Sigma \mu_i W_i$$

where μ_i are the mass absorption coefficient, and W_i are mass fractions of each element in the deposit. For the fine fraction of a typical urban aerosol, $\mu_L = 0.56\,\mathrm{cm^2\,mg^{-1}}$ for the geometry of our spectrometer (Dzubay, 1975).

Because of the manner in which sulfur is calibrated using copper sulfate aerosol particles, no correction is needed for attenuation of the X-rays by the filter medium. The 0.2 μm mass-median-diameter particles that were used in this calibration are similar in size to atmospheric particles that contain the fine particle sulfur. Thus the X-rays from the atmospheric particles and the calibration have approximately the same attenuation, and the effect cancels. According to measurements by Loo (1977) the attenuation factor for fine particles in 1.2 μm Millipore filters is 0.98 ± 0.02 for particles in the 0.03 to 1 μm size range, which indicates that such an attenuation effect is small and relatively independent of particle size.

In the coarse fraction, the particles are collected on the surface of the membrane filter, and for loadings below 500 $\mu\mathrm{g\,cm^{-2}}$ the particles form a monolayer. The attenuation factor for sulfur in the coarse fraction is $A = 0.64 \pm 0.22$. This value and values used for other elements are given by Dzubay (1975). Since the composition of the coarse particles in which the sulfur occurs is unknown, 0.64 was the median of values that were calculated for a variety of mineral and botanical particle matrices. The uncertainty in A represents the range of possible values for the coarse-particle attenuation factor.

Extraction procedure

After the EDXRF analysis had been completed, certain samples were selected for extraction and subsequent analyses. The extraction process consisted of removing the filter from its holder, loading it into an extraction vessel, filling the vessel with extraction solution, and then extracting by the use of an ultrasonic bath.

The filters arrived in the laboratory either held in holders with snap rings or bound to the holders. The filters were removed from the holders with tweezers in the first case or were cut from the holders with a sharp knife in the second. In either case the implements used were cleaned, rinsed, and allowed to dry after their use on each sample. The removal process was done as quickly as possible in order to prevent any contamination. For acidity measurements care was taken not to breathe on the filters to minimize exposure to exhaled ammonia. The filters were then placed in the extraction vessel with the back of each filter facing the bottom, to prevent any material from being inadvertently removed as the filter was inserted into the vessel.

The extraction vessel was a 30-ml Nalgene polypropylene bottle (Nalge, Inc., Rochester, NY) which

had been conditioned by soaking it in extraction solution for at least 8 h before use. To keep the filter submerged and open during extraction, a fluted Teflon pipe was placed in the vessel so that the fluted end rested on the outer, unloaded edge of the filter.

The volume of extraction solution used depended on the type and number of analyses performed and ranged from 8 to 20 ml. The extraction solution, perchloric acid, was obtained as 11.98 N from Baker Chemical Co. and was diluted to 5×10^{-5} N with distilled water. The extraction solution was delivered with 0.05% precision to the vessel by an Oxford Laboratories macro set pipet. The vessel was then capped and placed in an ultrasonic bath (Model 8845-60 Cole-Palmer Instrument Co., Chicago, Illinois) for 20 minutes. The ultrasonic bath tends to produce standing waves in the water so that regions exist where no agitation takes place. To overcome this problem the extraction vessel was continuously moved during the extraction period.

The above extraction procedure was used for analysis of SO_4^{2-}, NO_3^-, NH_4^+ and H^+. To determine the extraction efficiency, a set of 50 randomly selected extracted filters was reanalyzed by EDXRF. For the fine and coarse particle fractions, the extraction efficiencies for sulfur were found to be $98 \pm 1\%$ and $95 \pm 2\%$ respectively.

For those samples on which a sulfite determination was to be made, the extraction procedure was modified to minimize the conversion of sulfite to sulfite. We have demonstrated that carrying out the extraction at room temperature caused complete conversion of sulfite to sulfate. To prevent such conversion, a cold extraction process was developed. In the modified procedure the water bath was made up of a slurry of ice and water that maintained the temperature of the sample at 0°C during the extraction. With this procedure 90% of the sulfite was preserved.

Hydrogen ion analysis (H^+)

Titrimetry and a Gran's function plot were used to determine strong acidity (Brosset, 1976). The instrumentation included an Orion pH meter, a combination electrode, a Gran's function generator, and a Radiometer autoburett ABU 12. The data were recorded on a 1-mV strip-chart recorder. The Gran's function generator is an antilog amplifier (Model 755, Analog Devices, Norwood, MA).

The acid analysis procedure was as follows: (1) standardization of sodium hydroxide titrant, (2) measurement of the concentration of the acid extraction solution; (3) titration of extract using the 0.001 N NaOH, and (4) data analysis. Steps 1 and 2 were done once for each set of filter extracts or at least once each day. Nitrogen was bubbled through the solution being titrated to remove an interference by CO_2. The ionic strength of the volume being titrated was maintained at 0.02 M by the addition of KCl.

The method was characterized using 50 measurements on sulfuric acid standards that had a range of concentrations. The linear dynamic range was 10^{-6} to 10^{-4} M. The relative standard deviation was 2%, and the minimum detectable level was 1 nano-equivalent ml^{-1}.

Sulfate analysis spectrophotometric-thorin

The spectrophotometric-thorin method for sulfates was first described by Persson (1966) and later modified by Brosset (1975). With two exceptions, this method is identical to that described by Brosset; but instead of using dioxanes or acetone as a solvent, isopropanol is used and sulfonazo III (3, 6-*bis*-(*o*-sulfophenylazo)-4, 5-dihydroxy-2, 7-naphthalenedisulfonic acid) (Fisher Scientific) is used to obtain a reference intensity level.

Analysis was performed by using an autopipet (Autochem Instruments, Lindingo, Sweden) to automatically mix 1.8 ml of filter extract with 5 ml of 6.8×10^{-5} M barium perchlorate isopropanol solution and 0.4 ml of 1.37×10^{-3} M thorin solution in a 2 cm optical cuvette. The thorin solution was doped with H_2SO_4 to adjust the calibration to the linear range of the absorbance curve for the barium thorin titration (Brosset, 1975). Absorbance measurements at 520 nm are made using an Hitachi Model 101 spectrophotometer. The linear dynamic range of the method is from 0 to 6×10^{-5} M sulfate with a minimum detectable level of 2.5×10^{-6} M per ml. Analysis of 100 quality control solutions gave a relative standard deviation of 2%.

Ion exchange chromatography

Ion exchange chromatography is a relatively new technique for routine analysis of anions and cations in aqueous extracts of ambient aerosols. Mulik (1976) has described the application of a commercial liquid ion exchange chromatograph (IC) (Dionex Model 14, Sunnyvale, CA) to the analysis of water soluble anions. Before injecting a sample into the IC, 5 ml of the aerosol extract was spiked with a 1:1 mixture of 0.003 M $NaHCO_3$ and 0.0005 M Na_2CO_3 to adjust the molar CO_3^{2-} concentration to the range of 10^{-3}–10^{-5}. This basic mixture was added to neutralize the minute concentrations of perchloric acid used in the extraction procedure so that the injected solutions were approximately the molar concentration of the eluent used in the chromatograph. Because the instrument calibration curve was not linear, multipoint calibrations were performed over the range of concentrations expected in the samples. Since these samples were previously analyzed by EDXRF, the SO_4^{2-} calibration range could be adjusted accordingly. The signal from the IC conductivity detector was processed by a Hewlett Packard 3385A chromatographic control system. Peak areas and retention times were recorded to quantify and identify specific anions.

The relative standard deviations for mixtures of sodium nitrate and ammonium aqueous standards are shown in Table 2. Retention times and relative stan-

Table 2. Relative standard deviations for IC analysis of nitrate and sulfate standards

Molarity	Dionex attenuation setting	Standard deviation* SO_4^{2-}	Standard deviation* NO_3^-
1×10^{-4}	10	1%	1%
5×10^{-5}	10	0.3%	1%
1×10^{-5}	3	1.6%	1%

* Based on four consecutive injections of 0.4-ml volumes of standard solutions.

dard deviations were determined daily. The minimum detectable levels for sulfates and nitrates were 10^{-1} neq ml^{-1} and 5×10^{-2} neq ml^{-1} respectively. A typical IC chromatogram of an extract of a fine particle sample collected in Philadelphia is shown in Fig. 5. One notes the low nitrate concentration compared to sulfate. For almost all aerosol samples collected with the dichotomous sampler using Fluoropore filters, nitrate was always a small fraction of the sulfate concentration.

Ammonium analysis

The concentration of ammonium ions was determined with an ion selective NH_3 gas diffusion electrode (Orion Model 95-10). The response was recorded from a Corning-Digital 112 pH meter. Analysis was performed by mixing 7 ml of filter extract and 0.2 ml 5 N sodium hydroxide in a 20-ml glass beaker. The electrode was immersed into the solution with the tip extending approximately 1 cm into the solution. Readings were made between 2 and 3 min after immersing the electrode into the extract. When the sample concentration was less than 1×10^{-5} M, equilibration required as long as 5 min. The electrode was calibrated using dilute NH_4Cl standards (10^{-2} to 10^{-6} M). The minimum detectable level was 3 neq ml^{-1}. At concentrations above 10 neq ml^{-1} the relative standard deviation was $\pm 5\%$.

RESULTS AND DISCUSSION

Results of elemental and ionic analyses

In accordance with the objectives of this study, the mean concentrations for 18 elements and the mean total suspended particulate (TSP) masses of aerosol particles collected by dichotomous samplers at seven sites in the United States are presented in Table 3. The masses of the elemental concentrations represent unweighted arithmetic averages as determined by EDXRF. The means of the TSP represent unweighted arithmetic averages as determined by gravimetic measurements of the filtered aerosol. In some in-

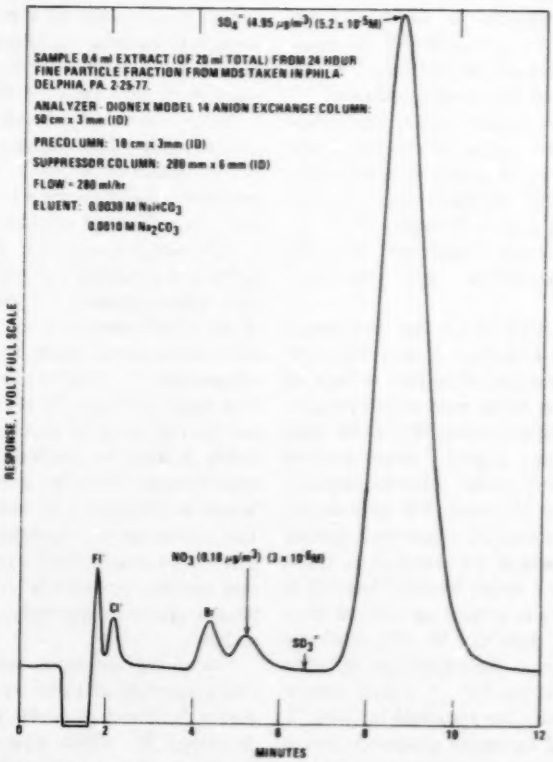
SAMPLE 0.4 ml EXTRACT (OF 20 ml TOTAL) FROM 24 HOUR FINE PARTICLE FRACTION FROM MDS TAKEN IN PHILADELPHIA, PA. 2-25-77.
ANALYZER - DIONEX MODEL 14 ANION EXCHANGE COLUMN: 50 cm x 3 mm (ID)
PRECOLUMN: 10 cm x 3mm (ID)
SUPPRESSOR COLUMN: 200 mm x 6 mm (ID)
FLOW = 200 ml/hr
ELUENT: 0.0030 M NaHCO3
0.0018 M Na2CO3
RESPONSE: 1 VOLT FULL SCALE
F⁻
Cl⁻
Br⁻
0
2
4
6
8
10
12
MINUTES

Fig. 5. Chromatogram of 0.4 ml extract of fine particles from a MDS operated on 25 February 1977 in Philadelphia (24-hour sample collection period). Concentrations of the sulfate and nitrate are expressed in molarity and in $\mu g\ m^{-3}$.

Table 3. Mean elemental concentrations (nanograms m^{-3}) and mean total suspended particulate (TSP) (micrograms m^{-3}) for two size fractions at several sites in the United States

Site	New York, NY 2/1977		Philadelphia PA 2–3/1977		Charleston W VA 4–8/1976 1/1977		St. Louis, MO RAMS 105 12/1975		Portland, OR 2/1977		Glendora, CA 3/1977	
Data	F*	C†	F	C	F	C	F	C	F	C	F	C
No‡	39	38	17	17	106	102	60	60	17	18	69	69
Al	129	840	48	642	262	1110	1983	8678	210	1175	<50§	331
Si	358	2018	262	1802	562	2616	412	4303	89	2808	188	995
P	173	120	57	40	42	33	218	583	55	104	24	30
S	5536	400	3096	454	3774	345	2774	752	1395	284	1612	240
Cl	227	607	115	225	144	232	145	180	478	719	72	719
K	273	185	137	165	97	279	200	324	153	190	100	179
Ca	358	1151	168	936	93	831	120	1910	67	765	99	442
Ti	<50§	41	21	61	11	81	36	74	18	146	10	42
V	207	81	60	11	<28	<28	23	29	29	19	5	<38
Cr	<25§	<15§	2	3	<28	<28	18	22	14	9	4	3
Mn	55	44	17	14	7	12	40	33	27	21	5	6
Fe	383	957	213	691	163	625	337	1001	187	946	124	360
Hi	57	18	30	7	0.6	0.3	15	10	42	10	14	3
Cu	73	31	25	7	25	29	59	16	62	17	12	6
Zu	373	85	148	38	30	20	147	74	61	30	45	16
Br	218	39	264	51	133	33	215	51	288	48	138	32
Sr	1	5	2	3	1	2	10	14	3	7	1	3
Pb	1057	170	945	170	623	134	833	243	866	174	614	92
TSP ($\mu g\ m^{-3}$)	64.5	42.6	31.4	17.5	33.1	23.4	NA‖	NA	20.9	27.6	NA	NA

* Fine fraction.
† Coarse fraction.
‡ Number of filters analyzed.
§ Average value less than detection limit, individual values exceeded detection limit.
‖ Not available.

stances, the arithmetic average was well below the detection limit for the element, in which case the detection limit is cited. The variability of detection limits from site to site reflects the differences in the flow rates and duration of the sampling periods.

We observe from these limited studies that vanadium concentrations were highest in the East coast areas where oil is used as the principal power plant energy source. For example, the mean vanadium concentration in New York City in February 1977 was 207 ng m^{-3}, while in South Charleston, WV, the mean vanadium concentration was less than 2 ng m^{-3}.

Figure 6 consists of plots of the fine and coarse sulfate concentration as a function of time. For New York City, 2-h concentrations of sulfate as high as 45 $\mu g\ m^{-3}$ were observed. At the peak sulfate concentration, the sulfate represented about 50% of the mass of the fine particle fraction. Figure 7 shows plots of the fine and coarse particle sulfur concentrations for RAPS sites 106 and 122 for nearly 100 days during 1975. Station 106 is located in a botanical garden a few kilometers northwest of the center of St. Louis and about 0.4 km from a major freeway. Site 122 is 45 km north of St. Louis in a rural agricultural area. The ADS sampler data show that for 94% of all the days sampled in St. Louis, the percentage of sulfur in the fine fraction exceeded 70%. A similar pattern appears for sulfur in the data presented in Table 3. Further examination of the mean concentrations of elements with atomic numbers above 12 shown in Table 3 reveals that sulfur is the most abundant element in the fine particle fraction.

Because the environmental effects and health effects of atmospheric sulfur are dependent upon its chemical form, it is essential to determine which sulfur compounds are present. If one assumes that all of the sulfur is in the form of sulfate, then using the data of Table 3, one can estimate the maximum possible percent of the sulfate associated with the various compounds indicated in Table 4. For each metal, the maximum possible percent is computed assuming that the entire observed amount of the metal occurs as a metal-sulfate compound; these results are given in Table 4. A summation of the maximum possible percent values indicates that no more than 10 to 30% of the sulfate can occur in the form of the assumed metal-sulfate compounds. The actual amount of such compounds is probably much less than this upper limit since Ti, Fe and Zn are likely to occur as oxides and lead is likely to occur as either an oxide or a halide. It must be concluded, therefore, that only a small fraction of the fine particle sulfur is chemically bound to elements with atomic numbers above 13. This conclusion is consistent with the measurements that will be described in a later paragraph that indicate that the atmospheric sulfur (assumed to be sulfate) is primarily associated with the cations NH_4^+ and H^+.

Further measurements were made to determine the oxidation state of sulfur in atmospheric particulate matter. Such measurements were made using recently developed IC, which separates anions on an ion exchange column with sufficient resolution to distinguish between SO_4^{2-} and SO_3^{2-}. Samples from South Charleston, Research Triangle Park, Philadel-

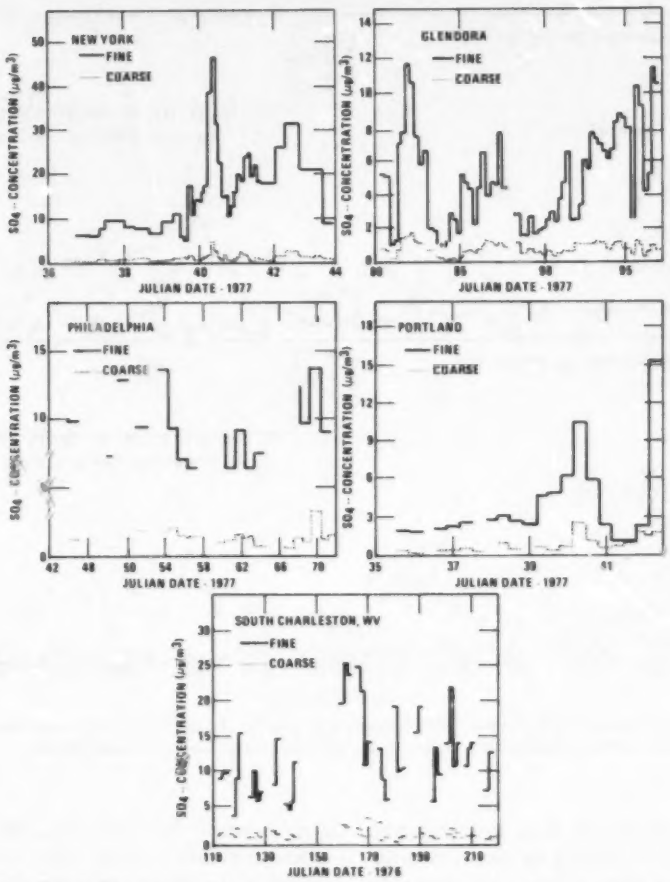

Fig. 6. The time history of equivalent sulfate concentrations in $\mu g\ m^{-3}$ as determined from EDXRF elemental analysis of dichotomous filter samples in two size fractions at five sampling sites in the US. The durations of the sampling periods are represented by the length of the horizontal lines, while the vertical lines connect consecutive sampling periods. The sampling periods were as follows: New York, 2 h; Phil., 24 h; South Charleston, 24 h; Glendora, 6 h; Portland, 4 h.

phia, and New York were analyzed, and in no case did the SO_3^{2-} exceed the minimum detectable level of $8\ ng\ m^{-3}$. In comparing the detection limit for sulfite with the mean sulfate concentration, one concludes that less than 0.1% of the sulfur in the filter extracts was in the form of sulfite. From the extraction efficiency studies, we determined that no more than 2% of the fine particle sulfur remained on the filter after extraction. If some of the nonextractable sulfur were a sulfite species, then sulfite could not account for more than 2% of the sulfur in the fine particle fraction.

Figure 8 shows a plot of water soluble sulfate measured by the IC versus total sulfur measured by EDXRF and plotted as sulfate. The data represent 18 randomly selected fine particle samples collected with manual dichotomous samples operated in South Charleston and Philadelphia during 1976 and early 1977. A linear regression analysis of the data reveals that:

$$SO_4^{2-}(IC) = 0.04\ \mu g\ m^{-3} + 0.98\ SO_4^{2-}(EDXRF)$$

and the correlation coefficient is 0.997. The ratio of the mean concentrations measured by IC and XRF is 0.988. This excellent agreement indicates that the measurements of water-soluble sulfate by IC and total sulfur by XRF are equivalent for the fine particle fraction.

A set of 18 randomly selected coarse particle samples was also analyzed for water-soluble sulfate by the IC and for total sulfur by EDXRF. A linear regression analysis reveals that

$$SO_4^{2-}(IC) = -0.30\ \mu g\ m^{-3} + 0.92\ SO_4^{2-}(EDXRF)$$

with correlation coefficient of 0.905. It is tempting to interpret the deviation of slope of the linear regression from unity as characteristic of the chemical species of sulfur found in the course particle mode. However, before such an interpretation can be made, possible sources of systematic error in the two techniques at low concentrations must be investigated. The coarse particle sulfate concentration in the present data are all below $2\ \mu g\ m^{-3}$ whereas the fine

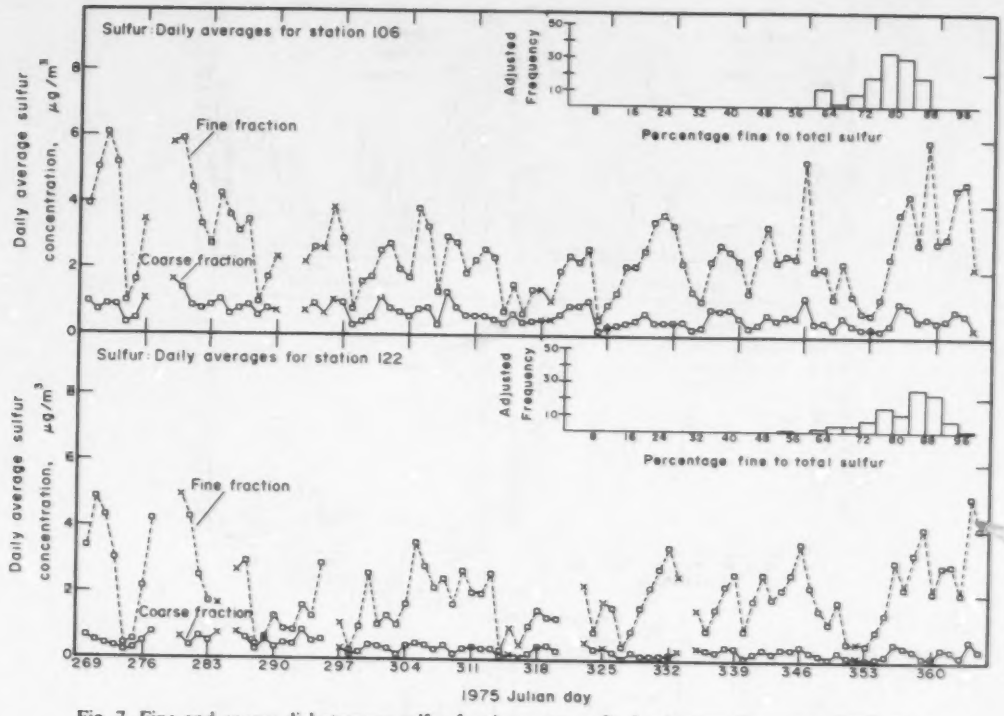
Sulfur: Daily averages for station 106
Daily average sulfur concentration, μg/m³
Fine fraction
Coarse fraction
Adjusted Frequency
Percentage fine to total sulfur
Sulfur: Daily averages for station 122
Daily average sulfur concentration, μg/m³
Fine fraction
Coarse fraction
Adjusted Frequency
Percentage fine to total sulfur
269 276 283 290 297 304 311 318 325 332 339 346 353 360
1975 Julian day

Fig. 7. Fine and coarse dichotomous sulfur fractions at two St. Louis sites. Frequency distribution of the ratio of fine particle sulfur to the fine plus coarse sulfur are also plotted.

particle concentrations were all above that value. The extraction procedures developed for the IC analysis were optimized for the sulfate concentrations expected for the fine particles. The appropriateness of these methods for the concentration ranges found in the coarse particle mode is currently being investigated. The relatively greater variability of the coarse particle data (correlation coefficient = 0.905) as compared to that of the fine particle data (correlation coefficient = 0.997) is indicative of the possibility that the combination of the sulfate with cations other than H^+ or NH_4^+ in the coarse particle mode may make a simple interpretation difficult. Work in progress to investigate these problems will be reported elsewhere.

Measurements of NH_4^+, H^+, SO_4, *and* NO_3^{2-}

Determinations of the H^+, NH_4^+, SO_4^{2-}, and NO_3^- concentrations were made using the Gran titration, ion selective electrode, thorin titration and IC. Such analyses were essential to characterize the sample, since the EDXRF analysis revealed that the metal cations were of minor importance.

Very few samples collected in our field studies over the past 18 months with the dichotomous sampler contained significant amounts of strong acid. In almost all instances the relationship between the NH_4^+ and SO_4^{2-} concentrations indicated that sulfate was in the form of ammonium sulfate. Only one aerosol sample out of over 120 collected in South Charles-

Table 4. Maximum possible percentages that various metal–sulfate compounds could contribute in the fine particle fraction. The percent sulfate values are computed from the data in Table 3 assuming that 100% of each metal is in the form of a sulfate compound

Compound	Maximum possible percent of total sulfate					
	New York	Phila.	Charleston	St. Louis	Portland	Glendora
K_2SO_4	2.0	1.8	1.1	3.0	2.0	2.5
$CaSO_4$	5.2	4.3	2.0	3.5	3.8	4.9
$Ti_2(SO_4)_3$	0.9	0.7	0.3	1.8	1.3	0.6
VSO_4	2.3	1.2	0.1	0.6	1.3	0.2
$Fe_2(SO_4)_3$	5.9	5.9	3.7	10.5	11.5	6.6
$ZnSO_4$	3.3	2.3	0.4	2.6	2.2	1.4
$PbSO_4$	3.0	4.7	2.6	4.6	9.6	5.9
Total	22.6	20.9	10.2	26.6	31.7	22.1

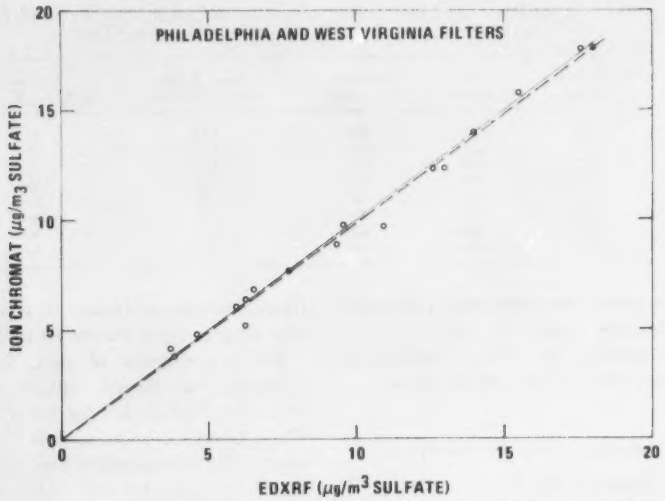

Fig. 8. A comparison of IC and EDXRF sulfate analyses for fine particles in 18 randomly selected samples.

ton contained detectable strong acid, and it only amounted to a few nanoequivalents. Aerosol samples collected during the winter of 1977 in Philadelphia and New York contained no detectable acidity. For these samples, no special effort was made to prevent neutralization of particles either during collection or during storage prior to analysis.

During July of 1977, aerosols were collected at Research Triangle Park with an automated dichotomous sampler designed to preserve the acidity of the samples. This ADS was equipped with a diffusion denuder to remove ammonia at the sampling inlet. After each sample was collected, the filter was immediately transferred within the ADS to a storage chamber that was continuously purged with nitrogen. When the filters were removed from the ADS, they were immediately transferred to a hermetically sealed ammonia-free chamber, where they remained until they were analyzed. The fine particle aerosol fraction was analyzed for H^+, NH_4^+ SO_4^{2-} and NO_3^-. The results, which are plotted in Fig. 9, reveal a significant amount of acidity. We attribute this detection of acidity to the precautions taken to preserve the integrity of the sample. Within the experimental error of the

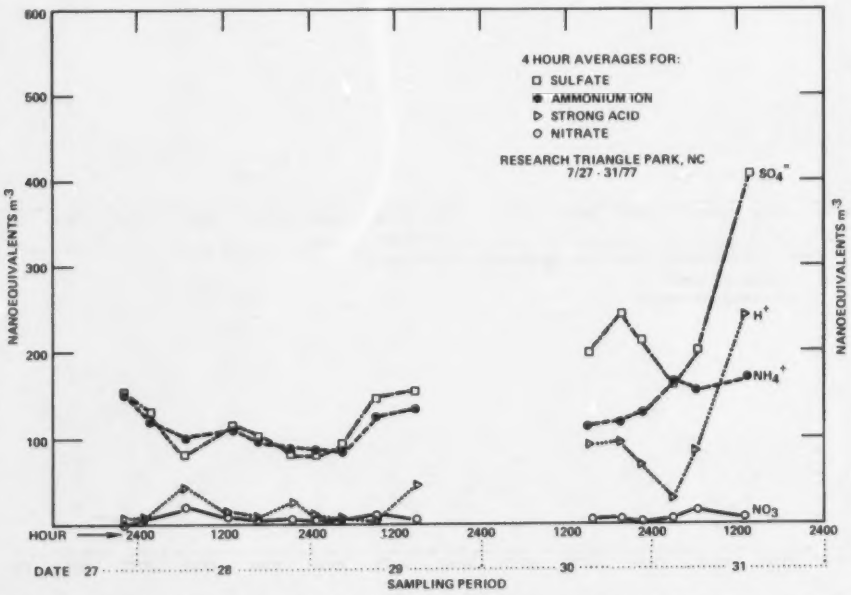

Fig. 9. Time series plot of the H^+, SO_4^{2-}, NO_3^- and NH_4^+ concentrations in fine particles collected with an ADS fitted with an NH_3 gas diffusion denuder and a sample preservation chamber.

Table 5. Summary of St. Louis sulfate concentrations ($\mu g\ m^{-3}$) determined by two methods for period September through December 1975

RAMS station number	Avg Hi-vol	Avg total dichotomous	Ratio Hi-vol total dichotomous	% Days fine S/total S > 0.70
106	11.0	8.9	1.23	97
108	12.7	10.0	1.27	79
112	10.6	9.2	1.23	95
115	9.6	7.8	1.23	99
118	9.9	6.6	1.50	83
120	9.9	7.3	1.35	100
122	8.9	6.2	1.44	94
124	9.8	6.4	1.53	89

measurements, the sum of the ammonium and hydrogen ion concentrations equals the sulfate concentration. In these samples, the nitrate concentration is a small fraction of the sulfate concentration.

Hi-volume and dichotomous sampler comparisons

As part of the Regional Air Pollution Study, Hi-volume samplers were operated at the Regional Air Monitoring Stations (RAMS) in St. Louis (Myers, 1975). At 10 RAMS stations, ADS were also operated. In the RAMS network, Hi-vols were operated for a 24-h period once every 3 days and the ADS were operated continuously. The fine and coarse fractions of aerosols collected with the ADS were analyzed for mass and elemental composition by beta gauge and EDXRF (Jaklevic, 1977) while aerosols collected with the Hi-vol were analyzed for mass and sulfate content (methyl-thymol blue method for sulfate). The average concentrations and ratios of concentrations for the two sampler types are shown in Table 5.

For a composite of eight RAMS stations the time-averaged Hi-vol sulfate concentration was $10.3\ \mu g\ m^{-3}$ while that for the dichotomous sampler (fine plus coarse fractions) was $7.8\ \mu g\ m^{-3}$. For every station the time-averaged concentration measured by the Hi-vol exceeded that measured by the dichotomous sampler. The discrepancy between the two methods ranged from 23 to 53%. No firm explanation of this preliminary result is offered. It is suggestive, however, of either aerosol sampling efficiency variations or possible sulfate artifact formation on the glass fiber filters of the Hi-vol. Figure 10 shows corresponding time series plots for total mass collected by ADS and Hi-vol at sites 106 and 122. The time-average value for the ratio of Hi-vol mass to total ADS mass at station 106 was 1.8. The corresponding ratio at station 122 was 1.2.

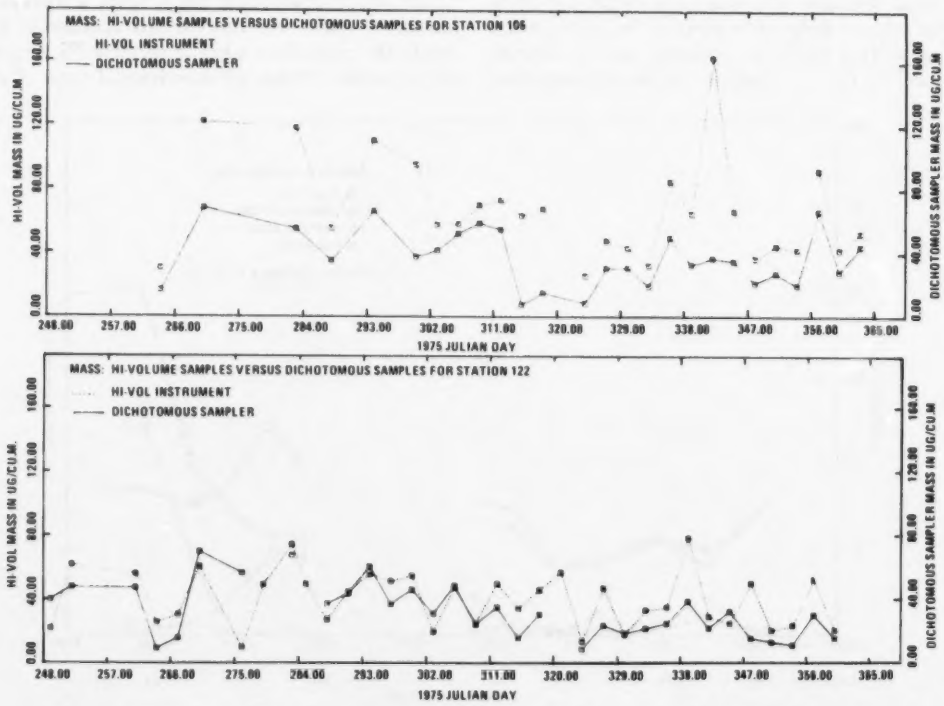

Fig. 10. Comparison of total mass concentrations measured by hi-vol and dichotomous sampler at two St. Louis sites.

In the RAMS stations, Hi-vols were operated from midnight to midnight and then automatically turned off. The filters were generally removed either the next day or in some cases 2 or 3 days later. Chahal (1976) has shown that a Hi-vol operated in this manner tended to pick up mass due to dust being blown into the sampler while it was idle and before the filter was replaced. This may partly explain why the Hi-vols operated in the RAMS network consistently showed higher mass loadings than the ADS.

CONCLUSIONS

The data presented represent the culmination of several years of intensive research to develop procedures and instrumentation to characterize the chemical form of sulfur in the atmosphere. These data definitively determine the chemical form of sulfur and serve to define several areas where further research on aerosols is needed.

Analysis by EDXRF and IC of aerosol samples collected with dichotomous samplers at six locations across the United States revealed that sulfur in particles $<3.5\ \mu m$ in aerodynamic diameter was in the form of sulfate. Analysis of randomly selected fine particle samples shows the ratio of the sulfate measured by IC and sulfur by EDXRF was 2.96 ± 0.15, which is in excellent agreement with the 3.00 value for pure sulfate. Other randomly selected samples analyzed by the IC showed that the sulfite levels were below the minimum detectable level ($8\ ng\ m^{-3}$). Based on these studies, EDXRF methods can now be considered a reliable analytical procedure to measure sulfate (as sulfur) in ambient aerosols.

Strong acid analysis of the fine particle fraction collected at a number of urban and rural areas in the United States consistently resulted in measurements below the minimum detectable level ($0.5\ ng\ m^{-3}$). This is likely due to neutralization of the acid on the filter either during sampling and/or subsequent handling. This conclusion is borne out by the immediately successful analysis for strong acid when the NH_3 denuder was used in conjunction with the modified ADS. It is important therefore when attempting to measure strong acid that precautions be taken to prevent neutralization.

This study shows that classical sampling methods are subject to a number of problems leading to erroneous measurements. For example, artifact formation caused by acid gas reaction with the filter and improper inlet design leading to collection of wind blown material may have caused misleading mass determinations. The dichotomous sampler with its inert filter medium and size fractionation has apparently overcome these difficulties.

Acknowledgements—The authors are indebted to Dr. William J. Courtney for his invaluable contribution in interpreting and formating the data from EDXRF measurements. The authors acknowledge the work of Dennis Reutter who fabricated the NH_3 denuder and was responsible for the collection and analysis of acid aerosols. We are indebted to the Northrop Services staff-particularly Carolyn Owen who assisted in data logging and reduction, and Edward L. Tew and Charles M. Kistler for providing the acidity, ammonium, and IC data cited in this report. In addition, we thank the West Virginia Air Pollution Control Board, William Ballanger, Ronald Patterson, A. P. Waggoner, and Robert Burton, for assisting in the operation of dichotomous samplers from which a majority of the data in this report were derived. Mass and elemental data for samplers collected with ADS in St. Louis were provided by the Lawrence Berkeley Laboratory.

REFERENCES

Arinc F., Gardner R. P., Wielopolski L. and Stiles A. R. (1976) Applications of the least-squares method to the analysis of XRF spectral intensities from atmospheric particulates collected on filters. *Advan. X-ray Analysis* **19**, 367–380.

Brosset C., Andreasson K. and Ferm M. (1975) The nature and possible origin of acid particles observed at the Swedish west coast. *Atmospheric Environment* **9**, 631–642.

Brosset C. and Ferm M. (1976) Man-made airborne acidity and its determination. IVL Publications B-34B. Gothenburg, Sweden.

Chahal H. S. and Romano D. J. (1976) High volume sampling: effect of windborne particulate matter deposited during idle periods. *J. Air Pollut. Control Ass.* **26**, 885–886.

Conner W. D. (1966) An inertial-type particle separator for collecting large samples. *J. Air Pollut. Control Soc.* **16**, 35–38.

Currie L. A. (1977) Detection and quantitation in X-ray fluorescence spectrometry. *X-ray Fluorescence Analysis of Environmental Samples*. pp. 289–306. Ann Arbor, Ann Arbor, Michigan.

Dzubay T. G. and Nelson R. O. (1975) Self absorption corrections for X-ray fluorescence analysis of aerosols. *Advan. X-ray Analysis* **18**, 619–631.

Dzubay T. G. and Stevens R. K. (1975) Ambient air analysis with dichotomous sampler and X-ray fluorescence spectrometer. *Environ. Sci. Technol.* **9**, 663–668.

Dzubay T. G., Stevens R. K. and Petersen C. M. (1977) Application of the dichotomous sampler to the characterization of ambient aerosols. *X-Ray Fluorescence Analysis of Environmental Samples*. pp. 95–105. Ann Arbor, Ann Arbor, Michigan.

Giauque R. D., Goulding F. S., Jaklevic J. M. and Pehl R. H. (1973) Trace element determination with semi-conductor X-ray spectrometers. *Analyt. Chem.* **45**, 671–681.

Goulding F. S., Jaklevic J. M. and Loo B. W. (1975) Fabrication of monitoring system for determining mass and composition of aerosols as a function of time. Environmental Protection Agency, Report No. EPA-650/2-75-048.

Hodgeson J. A., Bell J. P., Rehme K. A., Krost K. J. and Stevens R. K. (1971) Application of a Chemiluminescence Detector for the Measurement of Total Oxides of Nitrogen and Ammonia in the Atmosphere. Joint Conference on Sensing of Environmental Pollutants, Paper Number 71–1067, AIAA, New York, p. 197.

Jaklevic J. M., Goulding F. S., Jarrett B. V. and Meng J. D. (1974) Application of X-ray fluorescence techniques to measure elemental composition of particles in the atmosphere. *Analytical Methods Applied to Air Pollution Measurements* (Edited by R. K. Stevens.). pp. 123–146. Ann Arbor, Ann Arbor, Michigan.

Jaklevic J. M., Landis D. A. and Goulding F. S. (1976) Energy dispersive X-ray fluorescence spectrometry using pulsed X-ray excitation. *Advan. X-ray Analysis* **19**, 253–265.

Jaklevic J. M., Loo B. W. and Goulding F. S. (1977) Photon induced X-ray fluorescence analysis using energy dispersive detector and dichotomous sampler. *X-Ray Fluorescence Analysis of Environmental Samples*. pp. 3–18. Ann Arbor, Ann Arbor, Michigan.

Liu B. Y. H. and Kuhlmey G. A. (1977) Efficiencies of air sampling media. *X-Ray Fluorescence Analysis of Environmental Samples*. pp. 107–119. Ann Arbor, Ann Arbor, Michigan.

Loo B. W., Jaklevic J. M. and Goulding F. S. (1976) Dichotomous virtual impactors for large scale monitoring of airborne particulate matter. Fine Particles (Edited by B. Y. H. Liu), pp. 311–350. Academic Press, New York.

Loo B. W., Gatti R. C., Liu B. Y. H., Kim C. J. and Dzubay T. G. (1977) Absorption corrections for submicron sulfur collected in filters. *X-Ray Fluorescence Analysis of Environmental Samples*. pp. 187–202. Ann Arbor, Ann Arbor, Michigan.

Mulik J., Puckett R., Willians D. and Sawicki E. (1976) Ion chromatographic analysis of sulfate and nitrate in ambient aerosols. *Analyt. Lett.* **9**, 653–663.

Myers R. L. and Reagan J. A. (1975) The regional air monitoring system. St. Louis, MO, Proc. International Conference on Environmental Sensing and Assessment, Las Vegas, NV., 14–19 Sept.

Persson G. A. (1966) Automatic colorimetric determination of low concentrations of sulfate for sulfur dioxide in ambient air. *Air Wat. Pollut. Int. J.* **10**, 845–852.

Rickel D. G. and Dzubay T. G. Fitting of thin sample X-ray fluorescence spectra by a least-squares method. (To be published.)

Small J., Stevens T. S. and Bauman W. C. (1975) Novel ion exchange chromatographic method using conductimetric detection. *Analyt. Chem.* **47**, 1801.

Stevens R. K. and Dzubay T. G. (1975) Recent development in air particulate monitoring. *IEEE Trans. Nucl. Sci.* **NS-22**, 849–855.

Weiss R. E., Waggoner A. P., Charlson R. J. and Ahlquist N. C. (1977) Sulfate aerosol: geographic extent. *Science* **195**, 979–981.